

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-306192

(43)Date of publication of application : 17.11.1998

(51)Int.Cl.

C08L 33/06
B29C 45/14
B32B 27/30
C08J 5/18
C08L 51/04

(21)Application number : 10-053428

(71)Applicant : SUMITOMO CHEM CO LTD

(22)Date of filing : 05.03.1998

(72)Inventor : TADOKORO YOSHIO
TSUKUDA YOSUKE
HINO BETA KAZUO

(30)Priority

Priority number : 09 51770 Priority date : 06.03.1997 Priority country : JP

(54) FILM AND MOLDED ITEM PREPARED THEREFROM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a film or sheet excellent in thickness accuracy by using a compsn. which contains an acrylic polymer having a specified viscosity and a multilayered acrylic polymer.

SOLUTION: This film or sheet is formed from a compsn. comprising 20-90 pts.wt. acrylic polymer (A) having a reduced viscosity of 0.07 L/g or higher, 10-50 pts.wt. multilayered acrylic polymer (B) contg. a rubbery elastomeric layer, and 0-70 pts.wt. acrylic resin (C) having a reduced viscosity lower than 0.07 L/g, the sum of the three ingredients being 100 pts.wt. Pref., ingredient A comprises 10-90 wt.% methyl methacrylate units and 90-10 wt.% alkyl acrylate units. Ingredient B is pref. a three-layered polymer which comprises the innermost layer of a hard polymer formed mainly from methyl methacrylate, the intermediate layer of a soft rubbery elastomeric copolymer formed from a (4-8C)-alkyl acrylate and a polyfunctional monomer, and the outermost layer of a hard polymer similar to ingredient A.

LEGAL STATUS

[Date of request for examination] 15.02.2005

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a film or a sheet, and the Plastic solid that used it.

[0002]

[Description of the Prior Art] The injection-molding coincidence pasting approach is the shaping approach which is made to unite the film or sheet which is indicated by JP,63-6339,B, JP,4-9647,B, JP,7-9484,A, etc., and which was inserted between sex metal mold on the occasion of injection molding with the melting resin injected in a cavity, and is called the laminating method or the decalcomania method by the difference in the class of film which is decoration or the approach of painting and is used in a Plastic solid front face like.

[0003] Conventionally, as the film used for this injection-molding coincidence pasting approach, or a sheet, although the acrylic film or the acrylic sheet was known, it was not able to be said that the thickness precision was enough.

[0004]

[Problem(s) to be Solved by the Invention] Then, as a result of inquiring wholeheartedly so that this invention persons may develop the film or sheet of sufficient thickness precision, the film which consists of a resin constituent containing the specific acrylic polymer and specific multilayer-structure acrylic polymer of reduced viscosity resulted excelling in thickness precision in a header and this invention.

[0005]

[Means for Solving the Problem] (II) II [(I) and] That is, this invention contains the acrylic resin 0 which is the acrylic polymer 20 whose (I) reduced viscosity is 0.07 or more L/g - 90 weight sections, the multilayer-structure acrylic polymer 10 containing (II) rubber elastic layer - 50 weight sections, and (III) less than 0.07 L/g of reduced viscosity - 70 weight sections, and offers the film or sheet with which the total quantity which reaches (III) consists of a resin constituent which is the 100 weight sections.

[0006]

[Embodiment of the Invention] The reduced viscosity (value which dissolved 0.1g of polymers in chloroform 100ml, and was measured at 25 degrees C.) of (I) acrylic polymer used for the film or sheet (these are hereafter called the "film" collectively.), of this invention needs to be 0.07 or more L/g. In less than 0.07 L/g, in order for the melt tension at the time of film processing to fall, it becomes difficult to manufacture a film with a sufficient thickness precision, and they are 0.1 or more L/g preferably. Moreover, as for reduced viscosity, it is desirable that they are 0.25 or less L/g and 0.2 more L/g or less at the point that a film can be manufactured easily.

[0007] As this acrylic polymer, the acrylic polymer which consists of a methyl-methacrylate unit and an acrylic-acid alkyl ester unit, for example is mentioned. Here, as an alkyl group in acrylic-acid alkyl ester, the alkyl group of the carbon atomic numbers 2-10 is desirable, and an ethyl acrylate, acrylic-acid n-propyl, acrylic-acid isopropyl, acrylic-acid n-butyl, isobutyl acrylate, acrylic-acid hexyl, acrylic-acid octyl, etc. are mentioned as this acrylic-acid alkyl ester, for example. The methyl-methacrylate unit in an

acrylic polymer is 10 - 90 % of the weight, and, as for an acrylic-acid alkyl ester unit, it is desirable that it is 90 - 10 % of the weight. In addition, although the range of the glass transition temperature of this acrylic polymer is 40-100 degrees C in general, it is desirable that it is the range of 40-80 degrees C.

[0008] The content of the acrylic polymer in a resin constituent is 20 - 90 weight section. Since it is in the inclination a concave convex poor appearance becomes it easy to generate on a film front face to be under 20 weight sections, and it is in the inclination for the low film of surface hardness to be obtained when 90 weight sections are exceeded, it is not desirable practically.

[0009] (II) The multilayer-structure acrylic polymers containing rubber elastic layer are two-layer and an acrylic polymer which has the multilayer structure of three layers preferably at least. The range of the particle diameter of this acrylic polymer is usually 100-500nm. As a two-layer multilayer-structure acrylic polymer, a inner layer is soft rubber which the carbon number of an alkyl group becomes from the copolymer of the acrylic-acid alkyl ester of 4-8, and a polyfunctional monomer, and the thing based on the two-layer structure which is the hard polymer with which an outer layer uses a methyl methacrylate as a principal component is mentioned. Moreover, the thing based on the three-tiered structure which the hard polymer with which an innermost layer uses a methyl methacrylate as a principal component, and an interlayer become from the hard polymer with which the elastic rubber elastic layer which the carbon number of an alkyl group becomes from the copolymer of the acrylic-acid alkyl ester of 4-8 and a polyfunctional monomer, and the outermost layer use a methyl methacrylate as a principal component as an acrylic polymer of a three-tiered structure etc. is mentioned. What contains rubber elastic layer 20 to 60% of the weight especially is more desirable. This multilayer-structure acrylic polymer is indicated by JP,55-27576,B, JP,1-252653,A, etc. The content of this multilayer-structure acrylic polymer needs to be 10 - 50 weight section. Under 10 weight sections of impact strength are inadequate, or there is an inclination for the elongation of a film required for pasting shaping within metal mold not to be acquired. Since it is in the inclination for the surface hardness of a film to fall when 50 weight sections are exceeded, it is not desirable.

[0010] The film of this invention is desirable at the point that the film which may be carrying out 0-70 weight section content of this acrylic resin (III), and was excellent in this case with thermal resistance is obtained, although it is not necessary to consist of a resin constituent containing the multilayer-structure acrylic polymer containing the above-mentioned acrylic polymer and rubber elastic layer and the content of the acrylic resin whose reduced viscosity (III) is less than 0.07 L/g does not need to contain 0, i.e., this. What consists of 50 % of the weight or more of methyl-methacrylate units and less than 50 % of the weight of other vinyl system monomeric units more than a kind in which this and copolymerization are possible as this acrylic resin, for example is mentioned.

[0011] Here as a methyl methacrylate and a vinyl system monomer which can be copolymerized For example, ethyl methacrylate, methacrylic-acid butyl, cyclohexyl methacrylate, Methacrylic-acid phenyl, methacrylic-acid benzyl, 2-ethylhexyl methacrylate, Methacrylic ester, such as methacrylic-acid 2-hydroxyethyl A methyl acrylate, an ethyl acrylate, butyl acrylate, acrylic-acid cyclohexyl, Acrylic-acid phenyl, acrylic-acid benzyl, 2-ethylhexyl acrylate, Acrylic ester, such as acrylic-acid 2-HEDOROKISHI ethyl, an acrylic acid, Unsaturated fatty acid, such as a methacrylic acid, styrene, alpha methyl styrene, acrylonitrile, a methacrylonitrile, a maleic anhydride, phenyl maleimide, cyclohexyl maleimide, etc. are mentioned. In addition, the glass transition temperature of this acrylic resin is 80 degrees C or more in general.

[0012] The reduced viscosity of this acrylic resin is usually 0.03 or more L/g, and is the range of 0.03 - 0.065 L/g preferably.

[0013] (III) When reduced viscosity uses the acrylic resin which is less than 0.07 L/g, the content is usually more than 10 weight sections. Moreover, when the content exceeds 70 weight sections, it is in the inclination a concave convex defect becomes easy to produce on the front face of a film.

[0014] in addition, the content of the acrylic resin the acrylic polymer whose (I) reduced viscosity in the film of this invention is 0.07 or more L/g, the multilayer-structure acrylic polymer containing (II) rubber elastic layer, and (III) whose reduced viscosity are less than 0.07 L/g -- setting -- (I) and (II) -- and (III) the total quantity is the 100 weight sections.

[0015] The resin constituent in this invention may contain the usual additive. As this additive, weathering agents, such as a hindered phenolic antioxidant, the Lynn system antioxidant, a sulfur system antioxidant, an ultraviolet ray absorbent, and a hindered amine light stabiliser, a flame retarder, a coloring agent, a pigment, an inorganic system bulking agent, etc. are mentioned, for example. Although it is independent, or the ultraviolet ray absorbent of a benzotriazol system and a benzophenone system is generally mixed as an ultraviolet ray absorbent and it is used, the benzotriazol system ultraviolet ray absorbent of a viewpoint to the amount of giant molecules which lessens volatilization from a film and prevents degradation of a printing pattern is desirable.

[0016] What is necessary is to use acrylic (III) resin for the multilayer-structure acrylic polymer containing (I) acrylic polymer and (II) rubber elastic layer, or a pan for an extruder etc., and just to mix by approaches, such as melting kneading, in order to manufacture this resin constituent.

[0017] The film of this invention can be manufactured by the extrusion casting method by the chilled roll usually well known from this resin constituent, the extrusion method which both sides of a film are contacted to a roll surface, and fabricates them, the belt cooling extrusion method which both sides are contacted to a metal belt and fabricates them, the inflation extrusion method, the solvent casting method, etc. In this, the extrusion method which both sides of a film are contacted to a roll surface or a metal belt, and fabricates them, the approach of manufacturing with a belt cooling extrusion method, etc. are desirable also from a viewpoint of the printing omission prevention effectiveness which is the fall of about [that the film of a good surface state is obtained], and external Hayes, and the printing property of a pattern.

[0018] The film of this invention may be printed by one side, a pattern etc. may be used, it may be colored and it may be used. Moreover, what gave the configuration for the film by thermoforming, such as a vacuum forming, beforehand may be used for injection-molding coincidence pasting. Furthermore, the film of this invention may be used as an outermost layer of a multilayer film. That is, it is also possible to back other resin films, such as a vinyl chloride film and a transparence ABS film, on the film of this invention, and to consider as a multilayer film.

[0019] As for the thickness of the film of this invention, it is desirable that it is 0.1-0.6mm. The film of this invention is supplied towards the resin side by which melting injection is carried out after injection-molding metal mold in the field usually printed in the pattern etc. after having been printed by one side. That is, it is because it aims at taking out the depth of printing by the transparence (clear) layer with the condition of having become the last mold goods. For this reason, since feeling of depth, such as a printing shank, becomes scarce in less than 0.1mm, the thickness of this film is not desirable. Moreover, if it is going to carry out injection-molding coincidence pasting of this invention within metal mold industrially, the method which supplies a film in metal mold continuously is desirable. For that, since the thickness of this film is in the inclination it becomes impossible to roll by the shape of a continuous roll when it is desirable that it is 0.6mm or less and ** exceeds 0.6mm, it is not desirable.

[0020] As for the resin by which melting injection is carried out within metal mold at the time of injection-molding coincidence pasting of the film of this invention, it is desirable to choose ABS plastics or polycarbonate resin from viewpoints, such as the shock resistance of the final product done although ABS plastics, polycarbonate resin, polystyrene resin, or polyolefin resin is [like] usable mentioned above, and the stability of a dimension. Furthermore, when supplying a film continuously as industrial production, the thickness of a 0.1-0.2mm film is more desirable than reduction of volume weight, and the viewpoint of ***** at the time of a vacuum forming. Moreover, in the case of the film thickness exceeding 0.2mm, supplying in metal mold by **** is advantageous.

[0021] Injection-molding coincidence pasting using the film of this invention is performed to JP,63-6339,B, JP,4-9647,B, JP,7-9484,A, etc. like the approach of a publication. That is, by opening the female mold and male which form cavity space, inserting a film among both metal mold, closing both metal mold on both sides of a film in between, carrying out injection restoration and carrying out cooling solidification of the melting resin into a cavity, from a mold clamp meal and the gate, the front face of the injected Plastic solid is made to carry out the adhesion unification of the film, both metal mold is opened after that, and a Plastic solid is acquired. Conditions, such as resin temperature of

injection molding and an injection pressure, take the class of resin etc. into consideration, and are set up suitably.

[0022] Injection-molding coincidence pasting using this invention film is useful to a bumper or a garnish pan taking advantage of the descriptions, such as weatherability which methacrylic resin has, and surface hardness, surface gloss, as a process of paint substitutes, such as a sheathing member of home electronics, such as automobile interior members, such as automobile shell plate members, such as a side mall, a center console, and a door trim, an air conditioner, and a refrigerator.

[0023] Moreover, the film of this invention can be used taking advantage of the description of excelling in surface smooth nature, as a material of surface decoration techniques, such as printing by the ink jet printer using gravure, screen-stencil, or a computer graphics technique etc. Thus, the film with which it was printed prepares an adhesive layer in one side, and can use it for the surface decoration film of building materials, such as a display film for - advertising advertisement for sheathing (marking film), a chitin shell plate, and a table shell plate, etc. The adhesive layer in this case may be prepared in a printing side side, may be prepared in the opposite side of a printing side, and is selectable according to a display or the decoration purpose. Various kinds of alphabetic characters, a pattern, a photograph, etc. are printed, for example, this marking film can be used for the ornament of a passenger car, a bus, rail cars (an electric car, passenger car, etc.), etc., an annunciator, etc. Moreover, taking advantage of the weatherability which was excellent in methacrylic resin, it is useful on an outdoor signboard, a **** signboard, etc. This display film is excellent in weatherability (light) nature compared with the soft-polyvinylchloride-resin film which is the material of the marking film from the former, the polyurethane resin film, the PET film, etc. When it uses as a building-materials decoration film, the surface hardness and the surface gloss which are the description of methacrylic resin can serve as a big advantage.

[0024] Moreover, the film of this invention is usable also as an aiming at base material protection masking [/ the description referred to as excelling in transparency] film. Although the film which attached the binder layer to the polyethylene system resin film is used for the common masking film, it has the fault it is told to eye backlash whose polyethylene system resin is crystallinity that is easy to generate distortion optically translucent. The inspection of the masking film which has a binder layer on one side of this invention to it to the poor product by direct viewing is attained without removing a masking film, since it is transparent when it uses as masking films, such as a methacrylic resin plate and a polycarbonate resin plate. Moreover, when it uses as protection masking films, such as a polarization film and a phase contrast film, it becomes possible to measure directly characteristic inspections, such as an optical distortion or data JIESHON, without removing a masking film.

[0025]

[Effect of the Invention] The film of this invention can manufacture cheaply easily a molded laminate with the feeling of transparence which is excellent as the object for injection-molding coincidence pasting, or a film for a lamination, will maintain surface hardness if this film is used, and is deep.

Moreover, it can use for a masking film etc. preferably at a complex film, a marking film, and a pan.

[0026]

[Example] Hereafter, although an example explains this invention in more detail, this invention is not restricted at all by these examples. In addition, the evaluation approach is as follows.

(1) the time of shaping -- concavo-convex generating trial: -- the surface state of a pasting Plastic solid was observed visually, that in which O and detailed irregularity generated the good thing of a surface state was judged to be x, and the middle was judged to be **.

(2) Gauze abrasiveness : the fixture of Oriental Energy Machine factory friction tester D mold for colorfastness was equipped with gauze, the abrasion test of 500 round trips was performed by 200g of loads, and the visual judgment of the evaluation was carried out. It made O and to have worn out into x, and the middle was made into ** for not wearing out.

(3) Surface hardness : JIS K The pencil degree of hardness was measured according to 5400.

(4) Transparency : JIS K According to the approach of a publication, total light transmission (Tt) and Hayes were measured to 6718.

(5) Glass transition temperature (Tg) : the endoergic initiation temperature observed when a film sample

is heated with 10-degree-C programming rate for /by the differential scanning calorimetry (DSC) was searched for by the tangent method.

(6) Printing omission number : gravure of the pattern was carried out to film one side, width of face inspected visually by about 1m about the film which is about 10m, and die length converted the printing omission number into per two 1m.

(7) Thickness precision : measure average thickness (d0), the maximum section thickness, and the minimum section thickness for the thickness of a film with the dial gage of 1/1000mm precision about the cross direction and the 1m of the directions of taking over, and the difference of the maximum thickness and d0 or the difference of the minimum thickness and d0 is the value (deltad) of the larger one, and a formula (1) from d0 either.

Thickness precision (%) = $\text{deltad} / d_0 \times 100$ (1)

It was alike and thickness precision was searched for more.

[0027] The pellet 60 weight section of an example 1 acrylic polymer (they are manufacture, 85 % of the weight of methyl-methacrylate units, and 15 % of the weight of methyl-acrylate units by reduced viscosity 0.14 L/g and the bulk polymerization method), The multilayer-structure acrylic polymer [innermost layer of a globular form three-tiered structure The cross linked polymer of the methyl-methacrylate 37.5 weight section and the diallyl malete 0.075 weight section, The middle class The soft rubber elastic body of the butyl acrylate 38.5 weight section, the styrene 9 weight section, and the diallyl malete 0.95 weight section, acrylic polymer (JP,55-27576,B example 3 reference): which the outermost layer becomes from the copolymer of the methyl-methacrylate 14.4 weight section and the ethyl acrylate 0.6 weight section -- mean particle diameter -- the about 300nm]24 weight section and acrylic resin (it SUMIPEKKUSU-LG(s) the Sumitomo Chemical Co., Ltd. make --) The bead 16 weight section of reduced viscosity 0.06 L/g was mixed with the tumbler mold mixer, and with the twin screw extruder, melting kneading was carried out and it considered as the pellet. This pellet was extruded through T mold dice (600mm width of face) with a laying temperature of 255 degrees C using the 1 shaft extruder of 65mm of Toshiba Machine Co., Ltd. diameters phi of a barrel of make, it cooled so that a polishing roll might be completely touched in both sides, and the film with a thickness of 0.13mm was obtained.

[0028] The film with a thickness of 0.13mm obtained was put in in injection-molding metal mold (temperature of 50 degrees C), ABS plastics were injected in 3mm thickness to the rear face (the injection pressure of 1150kg/cm², resin temperature of 230 degrees C), and the Plastic solid (thickness of 3mm) with which the film was pasted together was acquired. The evaluation result of the film and Plastic solid which were acquired is shown in Table 1.

[0029] The same acrylic resin 37.5 weight section was mixed with having used in the bead 37.5 weight section of an example 2 acrylic polymer (they are manufacture, reduced viscosity 0.09 L/g, 87 % of the weight of methyl-methacrylate units, 3 % of the weight of methyl-acrylate units, and 10 % of the weight of butyl acrylate units by the suspension-polymerization method), the same multilayer-structure acrylic polymer 25 polymerization section of a globular form three-tiered structure as having used in the example 1, and an example 1 by the HENSHIERU type mixer, and with the twin screw extruder, melting kneading was carried out and it considered as the pellet.

[0030] This pellet was extruded through T mold dice (600mm width of face) with a laying temperature of 255 degrees C using the 1 shaft extruder of 65mm of Toshiba Machine Co., Ltd. diameters phi of a barrel of make, to the stainless steel belt side of a continuation stainless steel belt cooling system, as both sides of a film touched completely, they cooled, and the film with a thickness of 0.13mm was obtained. Subsequently, it was operated like the example 1 using the film with a thickness of 0.13mm obtained, and the Plastic solid was acquired. The evaluation result of the film and Plastic solid which were acquired is shown in Table 1.

[0031] Except only one side having contacted cooling of the film in example 3 example 2 on the polishing roll, and having performed it on it, it was operated like the example 2 and the film and the Plastic solid were acquired. An evaluation result is shown in Table 1.

[0032] The amount of the acrylic polymer used in example 4 example 2 was operated like the example 2 except making the amount of 20 weight sections and the acrylic resin used into 30 weight sections for

the amount of 50 weight sections and the multilayer-structure acrylic polymer used of a three-tiered structure, and the film and the Plastic solid were acquired. An evaluation result is shown in Table 1.

[0033] It replaces with the multilayer-structure acrylic polymer of example 53 layer structure. The multilayer-structure acrylic polymer [inner layer of two-layer structure The soft rubber elastic body of the butyl acrylate 38.5 weight section, the styrene 9 weight section, and the diallyl maleate 0.95 weight section, Except using about 300nm], mean particle diameter operates it like an example 4, and obtains a film. an outer layer -- copolymer [of the methyl-methacrylate 14.4 weight section and the ethyl acrylate 0.6 weight section] (it manufactured without forming innermost layer according to example 3 of JP,55-27576,B): -- The Plastic solid was acquired. An evaluation result is shown in Table 1.

[0034] It replaced with the example of comparison 1 acrylic polymer (reduced viscosity 0.09 L/g), and except having used the acrylic polymer (they being manufacture, 87 % of the weight of methyl-methacrylate units, 3 % of the weight of methyl-acrylate units, and 10 % of the weight of butyl acrylate units by reduced viscosity 0.06 L/g and the suspension method), it was operated like the example 2 and the film and the Plastic solid were acquired. An evaluation result is shown in Table 1.

[0035]

[Table 1]

| | T g (℃) | 鉛筆 硬度 | ガーゼ 摩耗性 | 光学特性 | | 成形凹凸 発生 | 印刷抜け 個数 (個/m ²) | 厚み 精度 (%) |
|-------|------------|----------|------------|------------|------------|------------|-----------------------------------|-----------------|
| | | | | T t (%) | ヘイズ (%) | | | |
| 実施例 1 | 73 | HB | ○ | 93 | 0.9 | ○ | 0.5 | 6 |
| 実施例 2 | 95 | HB | ○ | 93 | 0.4 | △ | 0.1 | 5 |
| 実施例 3 | 95 | HB | ○ | 92 | 2.5 | △ | 7.8 | 7 |
| 実施例 4 | 81 | HB | ○ | 93 | 0.8 | ○ | 0.4 | 8 |
| 実施例 5 | 80 | B | △ | 93 | 0.9 | ○ | 0.3 | 6 |
| 比較例 1 | 95 | HB | ○ | 93 | 0.4 | ○ | 0.2 | 14 |

[Translation done.]